Preparation and Properties of Vulcanizable Acrylic Ester-Acrylonitrile Copolymers

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EARLIER investigations at this Laboratory *(3, 6, 7, 8, 9)* resulted in the development of an acrylic elastomer called Lactoprene EV, which could be vulcanized to a rubberlike material with some unusual properties. This elastomer, a copolymer of 95 percent ethyl acrylate and 5 percent chloroethyl vinyl ether, was vulcanizable with sulfur and organic amines, such as Trimene Base.† The vulcanizates showed unusual resistance to heat and hot mineral oils as well as to atmospheric degradation and flexural breakdown. Commercial modifications, known as Hycar PA-21 and Hycar PA-31, have subsequently become available *(1, 11)*.

More recently another acrylic elastomer, a copolymer of butyl acrylate and acrylonitrile, called Lactoprene BN, was developed in this Laboratory *(4, 5)*. This new elastomer showed the desirable heat-resisting properties of Lactoprene EV; furthermore, the low-temperature properties and the resistance to swelling by boiling water were considerably improved over those of Lactoprene EV.

This paper reports the preparation of Lactoprene BN, the butyl acrylate-acrylonitrile copolymer, as well as other acrylate-acrylonitrile copolymers. A preliminary evaluation of the heat stability and the temperature of embrittlement of the vulcanizates is also reported.

Preparation of Polymers

Emulsion Polymerization: The method for emulsion polymerization was in general similar to that described previously *(8, 10)*. The preparation of the butyl acrylate-acrylonitrile copolymer, described below, is typical.

The acrylate monomer was purified by vacuum distillation in the presence of hydroquinone, and the redistilled monomer was freed of traces of hydroquinone by washing with cold dilute sodium hydroxide, followed by washing with water to remove alkali. The commercial grade acrylonitrile was distilled at atmospheric pressure.

The polymerization charge was as follows: Monomer, 100 parts; distilled water, 200 parts; emulsifier, 1-2 parts; and potassium persulfate, 0.02-0.03 part. Water and the emulsifying agent were charged into a three-necked flask fitted with a stirrer, reflux condenser, and thermometer. The monomer mixture was added, with continuous stirring, and the flask was heated by steam until the temperature of the contents was about 70° C.

Then 0.01 part of potassium persulfate was added, and heating continued. When the temperature of the charge reached approximately 87-91° C., vigorous polymerization set in. At this stage heating with steam was discontinued, and the reaction was kept under control by periodically cooling the flask with a stream of tap water. Even with as large a batch as 3000 g. of monomer, proper intermittent cooling permitted polymerization to proceed under reflux at a high rate but still under control.

When the vigorous polymerization had subsided (after approximately one-half hour), an additional 0.01 part of potassium persulfate was added, and the reaction was heated again by steam. This additional catalyst usually produced a further mild polymerization. A third 0.01 part of potassium persulfate was added after another one-half hour. The temperature of the refluxing emulsion generally rose to approximately 98° C., indicating almost complete polymerization had taken place. The temperature of the refluxing mixture was a valuable aid in following the course of polymerization, gradually increasing as monomer was consumed. Sampling of the polymerization mixture, as described under "Redox Polymerization," provided data for the approximate conversion curve (Fig. 1), from which it can be seen that approximately 70 percent of the monomer is converted to polymer in one-half hour.

When an attempt was made to prepare an emulsion containing 50 percent solids (87.5 percent butyl acrylate —12.5 percent acrylonitrile copolymer), considerable difficulty was encountered with foaming. Furthermore,
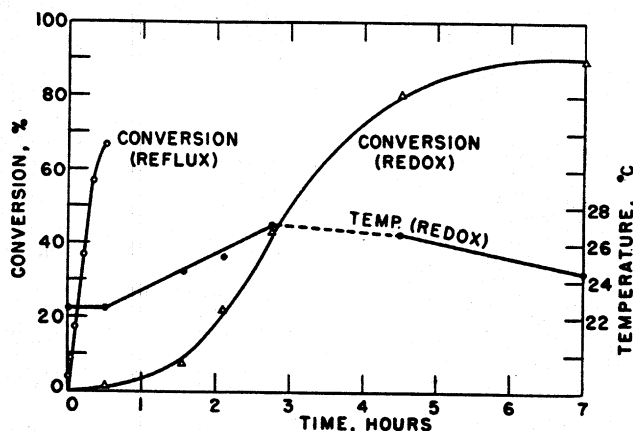

FIG. 1—Conversion curves for the polymerization of 87.5% butyl acrylate-12.5% acrylonitrile.

TABLE I—PREPARATION OF BUTYL ACRYLATE-ACRYLONITRILE COPOLYMER (LACTOPRENE BN)

Copolymer No.	Monomers, wt., % Butyl Acrylate	Acrylonitrile	Emulsifiers, % [a]	$K_2S_2O_8$, % [a]	Temp., °C [b]	Time, hrs.	Polymer Conversion, %	Yield, %	% Nitrogen in Polymer	Monomer Charge	Intrinsic Viscosity
1	95.0	5.0	Dupanol ME, 1	0.03	91-98.5	3.8	94	97	1.10	1.32	Insol.
2	90.0	10.0	Dupanol ME, 1	0.03	89-98.5	2.4	96	99	2.35	2.64	Insol.
3	85.0	15.0	Dupanol ME, 1	0.02	87-96	5.0	91	96	3.33	3.96	4.68
4	75.0	25.0	Dupanol ME, 1	0.03	83-96	3.0	96	101	6.24	6.60	Insol.
5	87.5	12.5	Dupanol ME, 1	0.03	88-98	2.8	94	98	2.75	3.30	4.81
6 [d]	87.5	12.5	Dupanol ME, 1	0.02	91-98.5	5.7	89	95	2.86	3.30	3.38
7 [e]	87.5	12.5	Dupanol ME, 0.5	0.03	88.5-96	2.8	83	91	2.54	3.30	4.10
8	87.5	12.5	Na Stearate, 2	0.06	90-97	2.0	71 [f]	75 [f]	3.07	3.30	2.35
9	87.5	12.5	Triton 720, 2	0.03	87-95	2.0	89	96	2.81	3.30	Insol.
10	87.5	12.5	Triton 720, 1 / Tergitol Paste No. 4, 1	0.05	88.5-97	2.5	92	97	3.01	3.30	Insol.
11 [g]	87.5	12.5	Dupanol ME, 2	Redox	22.5-27	7.0	91	91	2.46	3.30	Insol.

(a) 100% solids based on monomer; catalyst added in separate portions of 0.01%. (b) Initial and final temperature of refluxing polymerization mixture. (c) In acetone at 28° C. Insol. denotes presence of a gel component. (d) A semi-continuous polymerization: Monomers fed in one stream; H2O, emulsifier, and K2S2O8 (0.01%) fed in the other, over a period of 2.5 hours. Conversion at end of this stage was 73%. Heating with additional 0.01% K2S2O8 increased conversion to 89%. (e) Polymerization carried out in stainless steel vessel with brass and copper fittings. (f) Some loss of monomer during vigorous portion of polymerization. (g) Redox polymerization under N2. Initiated by 0.06% K2S2O8 and 0.03% NaHSO3.

the emulsion thickened so much that stirring was ineffective. The preparation of a 40 percent solids latex, however, was not so difficult, although considerable foaming occurred.

Unreacted monomer was next removed from the emulsion by passing live steam into the emulsion. During this stripping of monomer, the flask was heated externally by steam to minimize lowering the solids content by condensation. The emulsion was then broken by pouring it into an equal volume of 0.25 percent aluminum sulfate solution at approximately 50° C. The copolymer usually separated as a nice white granular material, which was thoroughly washed and finally dried at 50-55° C. in a circulating air oven. Some copolymers, particularly the copolymers of the acrylic esters higher than butyl, separated as a spongy mass; however, this was easily washed and shredded. Often when the polymer tended to precipitate as one large mass, this was prevented by adding about 1 gram of Dupanol ME to the aluminum sulfate solution prior to the addition of the emulsion. Table I summarizes the preparation of various butyl acrylate-acrylonitrile copolymers (Lactoprene BN). Table II summarizes the preparation of other acrylic ester-acrylonitrile copolymers. It can be seen that the yields, based on monomer actually consumed, are almost quantitative.

TABLE II—PREPARATION OF ACRYLIC ESTER-ACRYLIC NITRILE COPOLYMERS [a]

Copolymer No.	Monomers, wt., %		Temp., °C [b]	Time, hrs.	Polymer Conversion, %	Yield, %	% Nitrogen in Polymer	Monomer Charge	Intrinsic Viscosity [c]
12	Ethyl acrylate, 95	Acrylonitrile, 5	82-99	1.4	95	97	1.29	1.32	6.69
13	Ethyl acrylate, 90	Acrylonitrile, 10	82-96.5	1.7	93	97	2.51	2.64	5.98
14	n-Propyl acrylate, 95	Acrylonitrile, 5	85-97	3.3	95	97	1.35	1.32	Insol.
15	n-Butyl acrylate, 95	Methacrylonitrile, 5	92-98	1.5	95	96	1.05	1.04	Insol.
16	n-Butyl acrylate, 85	Methacrylonitrile, 15	93-99.5	5.0	93	94	2.98	3.13	2.73
17	n-Amyl acrylate, 95	Acrylonitrile, 5	94-97	3.5	89	93	1.28	1.32	Insol.
18	n-Hexyl acrylate, 91	Acrylonitrile, 9	87-96	3.5	81	96	1.69	2.38	Insol.
19	n-Hexyl acrylate, 90 [d]	Acrylonitrile, 10 [d]	20-30 [d]	5.8	96	98	2.03	2.64	3.67
20	n-Octyl acrylate, 90	Acrylonitrile, 10	91-97	3.5	96	98	2.11	2.64	Insol.
21	n-Octyl acrylate, 85	Acrylonitrile, 15	88-97	2.4	95	97	3.54	3.96	Insol.
22	n-Octyl acrylate, 80	Acrylonitrile, 20	83-97	4.0	90	94	4.88	5.28	Insol.
23	2-Ethylhexyl acrylate, 90	Acrylonitrile, 10	86-97.5	1.8	94	—	—	2.64	—
Terpolymers									
24	Ethyl acrylate, 10 / Butyl acrylate, 80	Acrylonitrile, 10	89-97	2.5	90	97	2.36	2.64	3.00
25	Ethyl acrylate, 20 / Butyl acrylate, 70	Acrylonitrile, 10	87-98	2.3	93	98	2.37	2.64	4.95
26	Ethyl acrylate, 40 / Butyl acrylate, 50	Acrylonitrile, 10	84-98	3.5	93	97	2.32	2.64	5.27
27	Ethyl acrylate, 10 / n-Octyl acrylate, 80	Acrylonitrile, 10	88-97	2.5	94	—	2.40	2.64	Insol.
28	Ethyl acrylate, 20 / n-Octyl acrylate, 70	Acrylonitrile, 10	86-98	3.0	94	—	2.45	2.64	Insol.
29	Ethyl acrylate, 30 / n-Octyl acrylate, 60	Acrylonitrile, 10	84-97	4.0	95	—	2.47	2.64	Insol.

(a) 1% Dupanol ME and 0.02-0.03% K2S2O8 (based on monomer), except Copolymers 15, 16, and 17, in which 0.05% K2S2O8 was used, and Copolymer 19 (footnoted). (b) Initial and final temperature of refluxing polymerization. (c) In acetone at 28° C. Insol. denotes presence of a gel component. (d) Redox polymerization under N2 with 0.06% each of K2S2O8 and NaHSO3 followed by an additional 0.06% each after 2.5 hours.

Recipe [a]	A	B	C	D	E	F	G	H	I	J	K	L
Copolymer	100	100	100	100	100	100	100	100	100	100	100	100
Carbon black (Furnex)	50	50	50	50	50	50	50	50	50	50	50	50
Carbon black (Philblack O)												
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1
Sulfur	0	0	1	0.5	0.25	0.75	0.5	0.5	0.5	1	1	1
Triethylene tetramine	1	2	0.5	0.5	1	0.75	1	1.5	2	1	1.5	2

Recipe [a]	M	N	O	P	Q	R	S	T	U	V	W
Copolymer	100	100	100	100	100	100	100	100	100	100	100
Carbon black (Furnex)	50	50	50	50	50	50	50				
Carbon black (Philblack O)								50	50	50	50
Stearic acid	1	1	1	1	1	1	1	1	1	1	1
Sulfur	1	2	3	4	5	3	4	1	1	1	1
Triethylene tetramine	2.5	1	1	1	1	1.5	2	1	1.5	2	2.5

(a) Ingredients given in parts by weight.

Reduction Activation ("Redox") Polymerization in Emulsion: The recipe used was 350 g. of butyl acrylate, 50 g. of acrylonitrile, 800 ml. of distilled water, 8 g. of Dupanol ME, 0.24 g. of potassium persulfate, and a total of 0.12 g. of sodium bisulfite (Copolymer 11, Table I). Potassium persulfate plus sodium bisulfite was first used by Bacon (2) as a reduction activation system to polymerize acrylonitrile. All the ingredients except the bisulfite were charged into a flask immersed in tap water (approximately 23° C.). The flask was equipped with stirrer, condenser, thermometer, and a nitrogen inlet tube; a stopcock sealed to the bottom of the flask facilitated sampling of the polymerization mixture. Nitrogen was then passed into the flask, and after 10 minutes 0.06 g. of sodium bisulfite was added. Forty minutes later an additional 0.06 g. of sodium bisulfite was added.

Seventy minutes after the first addition of bisulfite the polymerization began. It occurred smoothly, and no great evolution of heat was noted. The polymerization, which was followed by periodically withdrawing samples of the emulsion into a stopping solution of 1 percent hydroquinone and evaporating to dryness (Fig. 1), appeared to be completed after 7 hours. The emulsion was then steam-distilled. Only 3 g. of monomer was recovered. The polymer was obtained by pouring the latex into 0.25 percent aluminum sulfate. After drying, 362 g. (91% yield) of polymer was obtained.

A hexyl acrylate-acrylonitrile copolymer was also prepared by Redox polymerization (Copolymer 19, Table II).

Vulcanization of Polymers

These copolymers were relatively free of tack and were readily handled in the conventional rubber compounding equipment. As with Lactoprene EV, no initial breakdown was required. In general, the vulcanization procedure was similar to that described previously for Lactoprene EV (3) and Lactoprene BN (4, 5). The copolymer was masterbatched with carbon black and stearic acid in a hot Banbury mixer. Sulfur and triethylene tetramine were added on the mill. The recipes shown in Table III were evaluated in this study. The compounded stocks were aged for only 2 hours before curing at 298° F. for 60 minutes. A mold release agent was generally used to overcome any tendency to adhere to the mold.

Evaluation of Vulcanizates

The tensile tests were conducted according to ASTM specification D412-41; the die used was similar to die D except that the reduced section of the specimen was ¼-inch wide. The brittle points of the vulcanizates were determined by the method of Selker, Winspear, and Kemp (12). To determine the heat-aging characteristics of these vulcanizates, specimens were heated for 72 hours at 350° F. in a mechanical convection oven.

Discussion of Results

Polymerization: The copolymerization with acrylonitrile of the acrylates through butyl proceeded vigorously. In the higher acrylates, the rate of polymerization was noticeably more moderate. Increasing the acrylonitrile content of the monomer charge also resulted in moderation of the rate of polymerization. Copolymerization of butyl acrylate with methacrylonitrile (Copolymers 15 and 16, Table II) was considerably slower than the copolymerization with acrylonitrile. More catalyst, approximately 0.04 percent, was required to initiate the polymerization, and cooling was not necessary after the polymerization began. The conversion to polymer, however, was equally as good as with acrylonitrile. With a few exceptions, more than 80 percent of the acrylonitrile in the monomer charge entered into the polymer.

The polymerization could be satisfactorily conducted in a stainless steel vessel (Copolymer 7, Table I). The polymerization was also conducted on a semi-continuous basis by feeding the monomer in one stream and the aqueous phase, containing emulsifier and persulfate, in another stream (Copolymer 6, Table I). The two streams were fed to a flask heated by steam and containing a stirrer, condenser, and thermometer. By operation in this manner, the polymerization was conducted almost automatically and with no difficulty of control. The Redox polymerizations also were characteristically mild.

Tensile Properties: The initial tensile properties of the various vulcanizates are shown in Tables IV to VII. The tensile strengths were significantly lower than those of many butadiene stocks; however, the tensile strengths of most of these stocks were well above a serviceable minimum. The vulcanizates of the butyl acrylate copolymers (Tables IV and V) had substantially higher tensile strengths than the octyl acrylate copolymers of comparable acrylonitrile content (Table VI). Increasing the acrylonitrile content of the copolymers

TABLE IV—LACTOPRENE BN-12.5 COPOLYMERS[a]

Copolymer No.[b]	Raw Mooney	Vulcanizate[c]	Initial Properties Tensile Strength, psi.	Ultimate Elong., %	Modulus at 200%, psi.	Hardness[i]	Brittle Point, °F.	Aged 72 Hrs. at 350° F. Tensile Strength, psi.	Ultimate Elong., %	Modulus at 100%, psi.	Hardness[i]	Brittle Point, °F.
8[d]	37.5	J	1240	490	480	52	—11	1110	180	580	71	— 6
		K	1390	400	670	55	— 9	1150	150	750	75	0
		L	1330	200	1330	71	——	1340	80	0	86	——
		M	1360	180	——	73	——	1440	80	——	89	——
10[e]	37.5	J	1090	360	430	57	— 9	1050	170	530	68	0
		K	1270	260	1000	59	—11	1270	90	——	79	— 2
		L	1250	160	——	67	——	1420	70	——	87	——
		M	1410	170	——	69	——	1490	60	——	89	——
9[f]	39.8	J	1360	330	640	50	—24	1030	150	700	68	— 6
		K	1480	300	1000	53	—22	1280	110	1100	73	0
		L	1350	160	——	63	——	1390	80	——	83	——
		M	1400	140	——	68	——	1550	60	——	89	——
11[g]	32.5	J	1230	680	210	38	—27	1000	280	140	48	—22
		K	1380	420	500	44	—27	1050	160	480	61	—18
		L	1360	250	1100	51	—22	1200	110	1140	69	——
		M	1280	110	——	71	—22	1500	60	——	87	——
6[h]	37.5	C	Undercured									
		J	1400	260	1090	52	——	1280	120	1060	70	——
		K	1410	210	1360	59	——	1170	90	——	74	——
		L	1280	110	——	70	——	1580	60	——	86	——
5	34.0	C	900	560	190	35	——	1180	420	1506	42	——
		J	1340	390	510	45	—22	1400	210	540	59	——
		K	1260	190	——	58	——	1340	90	——	76	——
		L	1190	150	——	61	——	1390	80	——	79	——
7	37.8	C	Undercured									
		J	1280	300	690	50	—13	1140	140	660	63	——
		K	1150	200	1150	55	——	1190	100	1190	71	——
		L	1200	130	——	64	——	1330	60	——	83	——

(a) Lactoprene BN-12.5 is the copolymer prepared from a monomer charge of 87.5% butyl acrylate and 12.5% acrylonitrile. (b) Copolymer number corresponds to number of the polymer in Tables I and II. (c) Cures for 60 min. at 298° F. (d) Copolymer was prepared with Na stearate as emulsifier. (e) Triton 702 and Tergitol Paste No. 4 were used as emulsifiers in the polymerization. (f) Triton 720 was the emulsifying agent in preparing the copolymer. (g) Redox copolymer. (h) Semi-continuous polymerization. (i) Shore Durometer A.

TABLE V—OTHER BUTYL ACRYLATE COPOLYMERS AND TERPOLYMERS

Copolymer No.[a]	Monomer Charge	Raw Mooney	Vulcanizates[b]	Initial Properties Tensile Strength, psi.	Ultimate Elong., %	Modulus at 200%, psi.	Hardness[d]	Brittle Point, ° F.	Aged 72 Hrs. at 350° F. Tensile Strength, psi.	Ultimate Elong., %	Modulus at 100%, psi.	Hardness[d]	Brittle Point, °F.
1[c]	Butyl acrylate-95 Acrylonitrile-5	——	T	1230	470	470	58	—29	1160	310	410	71	—20
			U	1450	340	770	64	—29	1270	210	610	75	—18
			V	1480	250	1190	69	—29					
			W	1490	180	——	73	——					
1[c]	Butyl acrylate-95 Acrylonitrile-5	——	J	1120	480	380	54	—36	1070	230	300	54	—33
			K	1100	270	740	56	—33	870	120	660	63	—27
			L	1020	220	920	60	—31					
			M	730	150	——	63	—33					
2	Butyl acrylate-90 Acrylonitrile-10	——	G	1360	250	1020	55	—33	1240	140	——	67	——
			J	1400	270	990	56	—29	1190	130	——	70	——
			K	1250	190	——	60	—27	1190	100	——	76	——
			N	1395	280	970	56	—26	1290	130	——	71	——
3	Butyl acrylate-85 Acrylonitrile-15	52.5	D	1380	570	570	47	—17	1360	240	380	46	— 8
			G	1640	230	1450	60	—17	1660	100	1660	77	— 9
			H	1450	140	——	69	——	1720	60	——	87	——
			I	1430	90	——	75	——	1760	40	——	92	——
4	Butyl acrylate-75 Acrylonitrile-25	85.5	D	1880	240	1790	70	+21	2750	80	——	90	+43
			G	1960	140	——	78	——	2810	30	——	99	——
			H	2020	100	——	85	——	Too brittle to test				
			I	2100	60	——	92	——	Too brittle to test				
24	Butyl acrylate-80 Ethyl acrylate-10 Acrylonitrile-10	35.5	C	910	840	180	34	——	1070	550	130	41	——
			J	1280	390	550	48	—22	1160	200	400	56	—11
			K	1150	170	——	59	——	1210	90	0	71	——
			L	1120	140	——	60	——	1140	70	——	77	——
25	Butyl acrylate-70 Ethyl acrylate-20 Acrylonitrile-10	——	C	Undercured									
			J	1300	380	550	47	—20	1260	180	500	60	——
			K	1190	240	930	55	——	1200	120	980	71	——
			L	1150	150	——	60	——	1280	80	——	80	——
26	Butyl acrylate-50 Ethyl acrylate-40 Acrylonitrile-10	——	C	Undercured									
			J	1420	420	540	48	— 8	1380	210	500	60	——
			K	1350	240	1090	57	——	1360	110	1310	74	——
			L	1230	150	——	65	——	1370	70	——	85	——

(a) Copolymer number corresponds to the number of the polymer in Tables I and II. (b) Cured for 60 min. at 298° F. (c) The same copolymer was used with different carbon blacks. (d) Shore Durometer A.

TABLE VI—OCTYL ACRYLATE COPOLYMERS AND TERPOLYMERS

Copolymer No.[a]	Monomer Charge	Vulcanizate[b]	Initial Properties — Tensile Strength, psi	Ultimate Elong., %	Modulus at 200%, psi	Hardness[c]	Brittle Point, °F	Aged 72 Hrs. at 350° F. — Tensile Strength, psi	Ultimate Elong., %	Modulus at 200%, psi	Hardness[c]
20	n-Octyl acrylate-90 Acrylonitrile-10	A	Undercured								
		J	880	270	600	47	—51	390	70	—	66
		B	800	440	210	35	—	Too brittle to test			
		L	730	130	—	60	—	600	50	—	79
		G	760	420	370	44	—44	360	90	—	65
		E	970	250	740	50	—44	640	60	—	75
21	n-Octyl acrylate-85 Acrylonitrile-15	G									
		J	1100	260	780	52	—42	840	70	—	78
		F	960	300	540	45	—44	680	80	—	71
22	n-Octyl acrylate-80 Acrylonitrile-20	E	1300	150	—	65	—26	Too brittle to test			
		G	1280	150	—	67	—27				
		J	1310	130	—	71	—				
		F	1350	170	—	64	—27				
23	2-Ethylhexyl acrylate-90 Acrylonitrile-10	D	Undercured								
		G	Undercured								
		H	430	480	220	35	—	Too brittle to test			
		I	730	130	—	60	—				
27	n-Octyl acrylate-80 Ethyl acrylate-10 Acrylonitrile-10	A	610	570	150	30	—	Too brittle to test			
		B	630	310	300	37	—	Too brittle to test			
		J	950	370	440	45	—44	460	90	—	65
		L	950	220	870	54	—	600	70	—	75
		G	930	310	550	48	—44	390	70	—	70
28	n-Octyl acrylate-70 Ethyl acrylate-20 Acrylonitrile-10	A	580	700	150	32	—35	250	70	—	61
		J	990	340	290	45	—33	560	110	550	63
		B	650	460	210	35	—	Too brittle to test			
		L	990	110	—	67	—	790	30	—	85
		G	990	260	730	52	—33	390	30	—	70
29	n-Octyl acrylate-60 Ethyl acrylate-30 Acrylonitrile-10	C	Undercured								
		J	1190	360	580	47	—31	770	100	770	71
		K	1200	200	1200	59	—	910	50	—	81
		L	1180	120	—	68	—	1290	40	—	90
		N	1130	320	600	51	—24	750	90	—	75
		O	1070	340	580	51	—	840	80	—	75
		P	1110	350	600	50	—	840	80	—	75
		Q	1150	350	580	50	—	860	80	—	75
		A	690	590	250	40	—	Too brittle to test			
		G	1230	240	990	56	—24	800	70	—	77
		R	1290	140	—	75	—	1290	50	—	90
		S	1290	90	—	81	—	1300	30	—	96

(a) Copolymer number corresponds to number of the polymer in Tables I an II. (b) Cured for 60 min. at 298° F. (c) Shore Durometer A.

TABLE VII—MISCELLANEOUS ACRYLIC COPOLYMERS

Copolymer No.[a]	Monomer Charge	Raw Mooney	Vulcanizates[b]	Initial Properties — Tensile Strength, psi	Ultimate Elong., %	Modulus at 200%, psi	Hardness[d]	Brittle Point, °F	Aged 72 Hrs. at 350° F. — Tensile Strength, psi	Ultimate Elong., %	Modulus at 100%, psi	Hardness[d]	Brittle Point, °F
13	Ethyl acrylate-90 Acrylonitrile-10	58.6	C	1410	510	630	52	—	1400	440	580	62	—
			J	1540	310	1060	57	+27	1650	150	1290	77	+43
			K	1550	230	1390	60	+30	1950	90	—	84	+43
			L	1630	150	—	70	—	2440	60	—	94	—
12	Ethyl acrylate-95 Acrylonitrile-5	48.3	C	Undercured									
			J	1410	480	470	49	+16	1510	300	440	60	+25
			K	1400	300	830	56	+18	1520	150	1000	71	+27
			L	1360	210	1280	59	—	1590	110	1420	75	—
17	Amyl acrylate-95 Acrylonitrile-5	22.8	J	730	360	340	36	—45	610	200	140	41	—38
			K	760	300	430	39	—45	680	180	230	48	—42
			L	820	270	600	41	—	730	150	430	53	—
			M	400	140	—	46	—	760	110	540	62	—
18	Hexyl acrylate-91 Acrylonitrile-9		J	790	430	240	43	—49	280	100	280	56	—15
			K	740	200	740	56	—	800	110	750	67	—
			L	940	170	—	61	—	870	90	—	74	—
			L[e]	870	170	—	60	—	—				—
19[d]	Hexyl acrylate-90 Acrylonitrile-10		T	910	670	260	55	—	970	330	290	74	—
			U	1410	390	680	64	—	1110	150	780	84	—
			V[e]	1540	220	1390	74	—	1200	80	—	91	—
15	Butyl acrylate-95 Methacrylonitrile-5	24.0	J	Undercured									
			K	730	490	210	32	—36	690	360	30	37	—36
			L	760	480	230	36	—34	670	300	70	44	—31
			M	830	270	580	41	—	750	170	370	59	—
16	Butyl acrylate-85 Methacrylonitrile-15	28.0	J	450	600	340	45	— 9	530	300	380	62	— 6
			K	580	340	510	60	— 2	590	160	500	82	— 2
			L	700	270	620	68	—	670	130	610	87	—
			M	720	180	—	81	—	750	100	750	94	—

(a) Copolymer number corresponds to the number of the polymer in Tables I and II. (b) Cured for 60 min. at 298° F. (c) Cured for 30 min. at 298° F. (d) Redox copolymer. (e) Shore Durometer A.

appeared to increase the tensile strength (Table V); however, this did not appear to be true in the isolated example of the methacrylonitrile copolymer (Copolymers 15 and 16, Table VII).

In general, the tensiles decreased as the alkyl group of the acrylic ester increased. From previous experience and experiments with Copolymer No. 1 (Table V) and Copolymer No. 19 (Table VII), it is concluded that the tensile strengths can be substantially increased by replacing the Furnex with Philblack O. The tensile strengths of the copolymers of the higher acrylates, particularly octyl acrylate, were increased by replacing part of the higher acrylate with ethyl acrylate (Copolymers 27, 28, 29, Table VI). As compared with the ethyl acrylate-acrylonitrile and butyl acrylate-acrylonitrile copolymers, lower tensile strengths were shown by the copolymers of amyl, hexyl, n-octyl, and 2-ethylhexyl acrylates with acrylonitrile and by the butyl acrylate-methacrylonitrile copolymer. The hexyl acrylate-acrylonitrile copolymer, prepared by Redox polymerization, when loaded with Philblack O gave vulcanizates with tensile strengths as high as those of the butyl or ethyl acrylate copolymers. Thus, it appears evident that by suitable compounding these copolymers would produce vulcanizates with tensile strengths sufficiently high for many applications.

The tables show that the state of cure can be significantly altered by changes in the amine-sulfur ratio. In general, high amine concentrations resulted in vulcanizates with low elongations and fairly high hardness values. A minimal concentration of sulfur was necessary for the desired heat resistance; however, high sulfur concentrations apparently contributed little to the tensile properties of the vulcanizates. This is best illustrated by the vulcanizates of Copolymer No. 29 (Table VI). Vulcanizate J contained one part of triethylene tetramine and one part of sulfur. Holding the amine concentration to one part and increasing the sulfur concentration stepwise to 5 parts (Vulcanizates N, O, P, and Q) gave vulcanizates that had similar tensile properties.

Brittle Points of the Vulcanizates: The bend-brittle points of the green stocks (Tables IV to VII), were determined as described by previous investigators (12). The brittle point was dependent on the polymer composition increasing with higher acrylonitrile content and decreasing with the copolymers of the higher acrylic esters. The ethyl acrylate-acrylonitrile vulcanizates had brittle points from +16° F. (for the copolymer prepared from a monomer mixture of 95 percent ethyl acrylate and 5 percent acrylonitrile) to about +30° F. (for the copolymer prepared with 10 percent acrylonitrile) (Copolymers 12, 13, Table VII).

The brittle points of the copolymers of the higher acrylates were lower but were dependent on the acrylonitrile content of the copolymer, which was largely dependent on the acrylonitrile content of the monomer charge and to a less extent on the polymerization conditions. For example, a copolymer prepared from 95 percent butyl acrylate and 5 percent acrylonitrile (Copolymer No. 1, Table V) had a brittle temperature of about —33° F. The copolymers from a monomer mixture of 87.5 percent butyl acrylate and 12.5 percent acrylonitrile (Table IV) had on the average brittle points of about —11° F. These values were fairly independent of state of cure. Occasionally samples prepared with this same monomer composition had substantially lower brittle points. Thus, Copolymer Nos. 9 and 11 (Table IV) had brittle points of approximately —25° F. Chemical analysis indicated that the percentage of nitrogen in these samples was somewhat lower than in the other batches. Other copolymers, which have been expressly prepared with the least rise in temperature, also showed lower nitrogen values and, therefore, lower brittle points.

These observations suggest that the chemical composition of the copolymer has a more pronounced effect on the brittle point than structural variations such as branching within the copolymers.

Heat Resistance Characteristics: The resistance of acrylic rubbers to dry heat is now well known. The stress-relaxation studies of Tobolsky and coworkers (13) showed that heat resistance is dependent on two reactions—cross-linking and chain scission—which may occur simultaneously. Heat resistance is therefore dependent on the rates of these competing reactions. With acrylic vulcanizates, the heat resistance is also dependent on the vulcanizing ingredients. Dietz et al (3) demonstrated the importance of the compounding ingredients in achieving maximum heat resistance.

Since the change in the tensile properties is rather small when the vulcanizates are exposed to dry heat at 300° F. for periods less than one week, they were exposed to higher temperatures to demonstrate the effects of the compounding ingredients and the various acrylic ester copolymers on the heat resistance. In this Laboratory, it is customary to evaluate the tensile properties of the vulcanizates that have been exposed to dry heat for 72 hours at 350° F. If the tensile strength does not materially change and the ultimate elongation is above 100 percent, the vulcanizate is considered to have good dry-heat resistance. This was used as a criterion in comparing the dry-heat resistance of the various acrylic rubbers studied in this investigation.

The heat resistance data presented in Tables IV, V, and VII show that the acrylic vulcanizates had good heat resistance. The tensile properties of the ethyl through hexyl acrylate-acrylonitrile copolymers demonstrated that the amine-sulfur recipe controls the properties of the aged vulcanizates. The higher the concentration of triethylene tetramine in the recipe the tighter was the initial state of cure and the state of cure in the aged samples. The best heat resistance was obtained with the lowest concentration of the triethylene tetramine. Previous studies showed that sulfur is essential for maximum heat resistance; only small concentrations are required, however, and high concentrations of sulfur in the recipe produce no significant improvement over the lower concentrations.

The octyl acrylate-acrylonitrile copolymers did not have as good heat resistance as the lower acrylate ester copolymers. The data in Table VI illustrate the excessive decrease in elongation on exposure to dry heat at 350° F. for 72 hours. Replacing part of the octyl acrylate with ethyl acrylate did not materially improve the heat resistance of the vulcanizates, as illustrated in Table VI, Copolymer 29. The composition of the monomer mixture was 60 percent n-octyl acrylate, 30 percent ethyl acrylate, and 10 percent acrylonitrile, and none of the recipes yielded a vulcanizate with the heat resistance of the lower acrylate-acrylonitrile vulcanizates.

Copolymer Nos. 15, 16, Table VII, show the heat resistance of copolymers of butyl acrylate and methacrylonitrile. The initial tensile strengths were not particularly high which perhaps may be attributed to the method of polymerization. The relatively low raw Mooney values of these copolymers suggest that a substantial amount of low molecular weight components were present, thereby lowering the viscosity of the copolymer and also affecting the tensile strengths of the vulcanizates. The heat resistance was exceptionally good, however, since elongations well above 100 percent

were obtained after exposure to 350° F. for 72 hours. Replacing the Furnex carbon black with Philblack O would substantially increase the initial tensile strengths of the vulcanizates, which would in all probability be retained on heat aging.

Heat-Aged Brittle Points: In recent years a great deal of emphasis has been placed on the low temperature characteristics of synthetic rubbers, and considerable effort has been devoted to obtaining elastomers with brittle points well below —70° F. The acrylic rubbers described in this paper did not have particularly low brittle points; however, the brittle points of the heat-aged vulcanizates were substantially the same as those of the green vulcanizates, on the average being higher by only about 10° F.

Tables IV, V, and VII list the brittle points for many of the stocks aged at 350° F. for 72 hours. Apparently the change in the brittle point on aging is a good criterion for heat resistance, since many of the vulcanizates that exhibited the greatest change in brittle points also showed poor heat resistance. In particular, the hexyl acrylate-acrylonitrile copolymer (Table VII, Copolymer No. 18) had a brittle point for the green vulcanizates of —49° F.; however, on aging the brittle point changed to —15° F. In addition, the elongation of the vulcanizates also changed markedly on aging.

Summary

Copolymers of various acrylic esters, from ethyl to octyl, with 5 to 15 percent acrylonitrile or methacrylonitrile, were prepared by refluxing emulsion polymerization and in two instances by "Redox" polymerization. These copolymers were easily vulcanized with sulfur and triethylene tetramine recipes.

Heat-resistant vulcanizates were obtained from the copolymers of acrylonitrile with ethyl, butyl, amyl, and hexyl acrylates and also from the copolymer of methacrylonitrile with butyl acrylate. The octyl acrylate-acrylonitrile copolymers and the octyl acrylate, ethyl acrylate, and acrylonitrile terpolymers did not show similar heat resistance. Terpolymers obtained from ethyl acrylate, butyl acrylate, and acrylonitrile, however, produced heat-resistant vulcanizates.

The vulcanizates of lowest brittle points were obtained from the copolymers of the higher acrylic esters, but regardless of the acrylic ester used, the brittle point was considerably increased with increasing acrylonitrile content of the copolymer. The copolymers from 95 percent amyl acrylate—5 per cent acrylonitrile and the copolymer of 91 percent hexyl acrylate—9 percent acrylonitrile showed brittle points of —45° and —49° F., respectively. In general the brittle point of heat-resistant stocks did not change by more than approximately 10° F. on heat-aging for 72 hours at 350° F.

The butyl acrylate-methacrylonitrile copolymer appeared to have somewhat better heat-aging properties than did the butyl acrylate-acrylonitrile copolymer.

ACKNOWLEDGMENT

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